

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/CA05/000261

International filing date: 23 February 2005 (23.02.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/546,180
Filing date: 23 February 2004 (23.02.2004)

Date of receipt at the International Bureau: 07 July 2005 (07.07.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

PROVISIONAL APPLICATION COVER SHEET
Additional Page

PTO/SB416 (08-03)
Approved for use through 07/31/2006, OMB 0631-0032
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Docket Number		6013-150USPR IC/DP/mfr
INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle (if any))	Family Name or Surname	Residence (City and either State or Foreign Country)
Michael D.	Gulver	Ottawa, Ontario
Gilles P.	Robertson	Hull, Quebec
Pixiang	Xing	Gloucester, Ontario

(Page 2 of 2)

Number 2 of 2

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

13281 U.S. PTO
022304

METHOD FOR CROSS-LINKING SULFONATED POLYMERS
FOR THE PREPARATION OF PROTON EXCHANGE
MEMBRANES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This is the first application filed for the present invention.

BACKGROUND OF THE INVENTION

a) Field of the invention

[0002] The present invention relates to a new method for the preparation of proton exchange membranes (PEM) for fuel cells and, in particular, the method relates to the preparation of PEM based on cross-linked sulfonated polymers such as polyether ether ketone (SPEEK).

b) Description of the prior art

[0003] Fuel cells generate electricity directly from a fuel and an oxidant. The efficiency of fuel cells is not thermodynamically restricted and greatly surpasses the efficiency of conventional power generation devices since it does not involve fuel burning. Fuel cells consist of two catalytic electrodes (an anode and a cathode) separated by an electrolyte. The electrolyte can be a liquid, such as alkaline or H_3PO_4 , or a solid, such as a proton exchange membrane (PEM). In PEM fuel cells, the fuel is oxidized electrochemically to positive charged ions on a first electrode. The protons diffuse across the PEM to recombine with the oxygen ions at the surface of the other electrode. The electron current flowing from one electrode to the other through an external load produces power.

[0004] The PEMs separating the electrodes in a fuel cell should have low resistance to diffusion of ions from one electrode to the other. However, they must provide a barrier against the fuel and oxidant cross-leaks keeping them apart. Diffusion of leakage of the fuel or oxidant gases across the membrane leads to power losses and other undesirable consequences. PEM should also have a high resistance to the

electron flow. Therefore, if the device is even partially shorted out, the power output is reduced.

[0005] For reasons of chemical stability, perfluorosulfonic membranes, such as the commercially available Nafion™, are widely used both in fuel cell research and industry. They however suffer from several shortcomings among which their high cost presents a major obstacle on the way toward commercialization. Moreover, a conductivity loss occurs above 80°C and it has a low stability toward alcohols which imposes restrictions on the fuel selection. Recently, many efforts have been undertaken to develop hydrocarbon based alternatives to Nafion™, which would be less expensive and free from disadvantages of fluorinated membranes. Among the various membranes with various mechanical and electrical properties, long-term stability, efficiency and cost that emerge over the last years, the membranes based on polyether ether ketone (PEEK) have shown considerable promises [G. Pourcelly and C. Gavach, Perfluorinated Membranes, in Ph. Colomban (Ed.) Proton Conductors: Solids, Membranes and Gels-Materials and Devices, Cambridge University Press, New York, 1992, pp. 294-310; O. Savadogo, Emerging Membranes for Electrochemical Systems: (I) Solid Polymer Electrolyte Membranes for Fuel Cell Systems, J. New Mat. Electrochem. Syst., 1, 1998, 66; T. Kobayashi, M. Rikukawa, K. Sanui, N. Otega, Proton Conducting Polymers Derived from Poly(Ether- Ether Ketone and Poly(4-phenoxybenzoyl-1,4-Phenylene), Solid State Ionics, 106, 1998, 219; J. Kerres, A. Ullrich, and Th. Haring, New Ionomer Membranes and their Fuel Cell Application: 1. Preparation and Characterization, 3rd Int. Symp. on New Materials for Electrochemical Systems, Montreal, Canada, July, 1999, 230; S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, and S. Kallaguine, J. Membr. Sci, 173, 2000, 17; B. Bonnet, D.J. Jones, J. Rosière, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, B. Bauer, A. Peraio, and E. Ramunni, J. New Mat. Electrochem. Syst., 3, 2000, 87]. They have good thermal stability, appropriate mechanical strength, and a high proton conductivity which depends on the degree of sulfonation. However, the mechanical properties of PEEK progressively deteriorate with sulfonation [X. Jin, M.T. Bishop, T.S. Ellis, and F.E. Karasz, British Polym. J., 17, 1985, 4]. Therefore, the long term stability of the highly sulfonated polymer is questionable. The structural weakness of uncross-linked sulfonated polymers

initiated several attempts to prepare more stable and mechanically stronger cross-linked PEMs. Sulfonated PEEK (SPEEK) is a convenient polymer to be cross-linked since it can be achieved through bridging links to the very reactive sulfonic acid functions. The first cross-linking of SPEEK was carried out using suitable aromatic or aliphatic amines [US Patent 5,438,082]. The use of a similar cross-linker also having terminal amide functions which forms imide functionality through a condensation reaction with the sulfonic acid groups of SPEEK was proposed [US Patent 6,090,895]. The imide group is supposed to be acidic and therefore able to participate in the proton transfer, thus contributing to the conductivity of the polymer.

[0006] Cross-linking of SPEEK can be performed through intra/inter chain polymerization of sulfonic acid functionalities allegedly initiated simply by appropriate thermal treatment [US Patent 5,795,496].

[0007] The cross-linked SPEEK membranes were found to be much less susceptible to swelling than uncross-linked SPEEK. They are comparable to commercial Nafion™ in terms of their mechanical strength, stability and proton conductivity. However no fuel cell performance data are available in the literature yet. Furthermore, when amine functions are used to attach a cross-linker to sulfonic acid groups, sulfanilamide is produced [US Patents 5,438,082 and 6,090,895]. The hydrolytic stability of sulfanilamide is questionable and casts doubts upon the membrane durability under fuel cell operating conditions.

SUMMARY OF THE INVENTION

[0008] Accordingly, an object of the present invention is to provide a proton conducting polymer that is mechanically and chemically stable.

[0009] Yet another object of the present invention is to provide a membrane having a high proton conductivity, low electronic conductivity, which is mechanically strong and chemically stable and can prevent the cross-leaks of molecular gases.

[0010] Still another object of the present invention is to provide a new method to produce a proton conducting polymer for fuel cells which permits to increase the membrane stability and to reduce the methanol transfer through the polymer.

[0011] The present invention is a method for the preparation of a cross-linked proton exchange membrane. The method comprises:

providing a sulfonated polymer;

dissolving the polymer in a polar casting solvent;

adding at least one cross-linker agent of one of polyol and diol types, the cross-linker agent is added in a sufficient ratio of polyol molecules per repeat unit of the sulfonated polymer to generate cross-linking;

casting the solution to obtain the membrane; and

curing the membrane

[0012] The present invention also concerns a cross-linked proton exchange membrane prepared in accordance with the method described above.

[0013] It further relates to a fuel cell using a cross-linked proton exchange membrane prepared in accordance with the method described above.

[0014] The present invention also relates to a new method for the preparation of proton exchange membranes based on cross-linked sulfonated polymers, preferably cross-linked poly ether ether ketones (SPEEK). The method of the present invention consists in thermally activating the bridging of the polymer chains with diols or polyols as cross-linkers. The addition of diols or polyols makes the resulting polymer stronger and reduces its swelling by water without a substantial reduction in proton conductivity. It also concerns proton exchange membranes made by the method of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Further features and advantages of the present invention will become apparent from the following detailed description, taken in combination with the appended drawings, in which:

[0016] FIG. 1 is the sulfur content in cross-linked SPEEK membranes as function of the treatment temperature: (a) the degree of sulfonation (DS) is determined by titration and the sulfur content is calculated, (b), (c), and (d) the sulfur content is determined by elemental analysis and the DS is calculated, (e) the DS is determined by H^1 NMR and the sulfur content is calculated;

[0017] FIG. 2 is a possible reaction of SPEEK cross-linking;

[0018] FIG. 3 is the preparation formulations of different SPEEK samples; and

[0019] FIG. 4 is the swelling and the conductivity of cross-linked SPEEK membranes as function of the DS measured by titration, the values in brackets are the [ethylene glycol] / [SPEEK] molar ratios used in the membrane preparation.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0020] The present invention relates to a method for the preparation of reticulated sulfonated polymer membranes that can be used as proton conductive membranes in proton exchange membrane (PEM) fuel cells.

[0021] Usually, the first step to provide an inexpensive dried sulfonated polymer to form a membrane layer is to sulfonate an appropriate polymer. The preferred starting material is a polyether ether ketone (PEEK), which is a temperature resistant and oxidatively stable engineering polymer. However, any other appropriate polymer that can be sulfonated could be used. Several sulfonation techniques are well-known by those skilled in the art. A sulfonation technique is described in example 1 but any appropriate technique can be applied. Polymers having a high degree of sulfonation (DS), i.e. above 0.6, are preferred.

[0022] The second step is to dissolve the dried sulfonated polymer obtained in a polar organic solvent such as N,N-dimethylacetamide (DMAc), dimethylformamide

(DMF), N-methyl-2-pyrrolidone (NMP), butyrolactone, water-acetone, water-alcohol mixtures or a polar inorganic solvent such as water. A diluted solution is thus obtained wherein the sulfonated polymer concentration varies between 10 and 15 wt%. The diluted solution is usually cast at room temperature and then cured under vacuum at 25-150° C for few days.

[0023] However, as it will be shown in the following examples, a thermal treatment is not sufficient to induce any significant cross-linking of pure SPEEK materials. Indeed, pure SPEEK materials having a high DS cast at room temperature from the above-mentioned solvents remain soluble in these solvents after drying and curing under vacuum at 120-150° C for several days. This observation is contradictory with previous assertions [US 5,795,496] stating that heating SPEEK materials having a high degree of sulfonation (DS) to 120° C is sufficient to initiate thermal cross-linking.

[0024] Experimentations showed that high DS SPEEK materials heated up to 250° C under vacuum resulted in membranes which are insoluble in any solvent (except H₂SO₄) and stable in boiling water. In some instances this thermally induced transformation started at 220° C. The chemical analysis of the samples also showed that heating above 200° C brought about desulfonation of SPEEK accompanied by SO₃ release. FIG. 1c presents the results of the elemental analysis for sulfur for pure SPEEK membranes cast from a NMP solution and treated at different temperatures. More details on the various characterization tests are given below. The sample studied had a DS of 0.94 according to nuclear magnetic resonance (NMR) analysis (see Table 1) which should correspond to a calculated value of 8.2 wt% of sulfur. From the plot, it can be seen that the initial sulfur content (Sample 4d dried at 100° C) obtained by chemical analysis is 9% lower than the value calculated from NMR. Heating to 200° C reduced the discrepancy between the results of these two analytical techniques. It suggests that this difference was associated with the presence of residual NMP solvent in the membrane. NMP is however difficult to remove completely as its boiling point is 202° C. Heating above 200° C under vacuum strongly reduces the sulfur content below the values corresponding to a DS of 0.5, as shown in Fig.1c. These SPEEK samples become insoluble in any solvents and might be mistaken for thermally cross-linked. However, treated under vacuum at

150° C for several days these SPEEK membranes remained soluble and did not show any properties of cross-linked polymers.

[0025] In the present invention, a certain amount of a polyol (or polyatomic alcohol) cross-linker such as glycerol (or glycerin), ethylene glycol and meso-erythritol is added to a diluted sulfonated polymer solution. As mentioned above, a polar organic or inorganic solvent is used to dilute the sulfonated polymer. The concentration of the diluted solution varies between 5 and 25 wt%, preferably between 10 and 15 wt%. More concentrated solutions produce thicker films while less concentrated produce thinner films. The solution is then agitated for a sufficient amount of time and degassed. The degassed polymer solution is cast and dried at ambient temperature. The dried polymer is then cured under vacuum at a gradually increasing temperature. Preferably, the temperature increases between 25 and 180° C.

[0026] As it will be explained more in details later, cross-linking is observed when the casting medium contained a certain amount of a diol or polyol: the membranes changed of color and became mechanically strong and insoluble in any solvent used. Cross-linking generally occurs when the ratio of diol or polyol to sulfonated polymer is at least one molecule per repeat unit of polymer. FIG. 2 shows the chemical reaction assumed to be involved in such cross-linking.

[0027] Several examples were carried out to analyze the effect of polar organic and inorganic solvents and polyol cross-linkers on the cross-linking of a sulfonated polymer.

Example 1 – PEEK Sulfonation

[0028] PEEK extrudate samples were first provided. The PEEK samples used for this example are PEEKTM produced by Victrex[®]. Typically 20g of PEEK was dried in a vacuum oven at 100° C and then dissolved in 500ml of concentrated (95-98%) H₂SO₄ sulfuric acid at 50-90° C under vigorous mechanical stirring to produce a polymer solution. The reaction time ranged from 1 to 6.5h. To stop the sulfonation reaction and produce a polymer precipitate, the polymer solution was decanted into a large excess of ice-cold water under continuous mechanical agitation. The polymer

precipitate was filtered and washed several times with distilled water until the pH was neutral. The polymer was then dried under vacuum for 1-2 days at 25-40° C to give a dry SPEEK polymer. The degree of sulfonation was determined by nuclear magnetic resonance (NMR) analysis ¹H NMR in accordance with techniques known in the art.

Example 2 – Membrane Preparation

[0029] The dried SPEEK polymers were dissolved in one of the following solvents: DMAc, DMF, NMP, water-acetone or water-alcohol mixtures to a 10-15 wt% SPEEK solution. An amount of a diol or polyol cross-linker was added to the SPEEK solution agitated for 30 minutes. Glycerol, meso-erythritol and ethylene-glycol cross-linkers were added in different samples of the diluted SPEEK solution. Then, the solutions were degassed for 30 minutes and cast onto a glass plate. The cast solution were dried under ambient conditions for several days and then cured under vacuum at 25-150° C for a few more days.

[0030] FIG. 3 lists the preparation formulations of the different SPEEK samples tested.

Example 3 – Characterization of SPEEK membranes

[0031] The glass transition temperature (T_g) of the SPEEK membranes was established using a DuPont 910 differential scanning calorimeter (DSC) at a heating rate of 10° C per minute. The thermo-gravimetric analysis (TGA) was carried out using a DuPont 951 thermobalance controlled by a 2100 analysis station. Specimens were heated to 900° C at a rate of 10° C per minute under a nitrogen atmosphere. The ¹H-NMR spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz. For each analysis, a 2-5 wt% polymer solution was prepared in DMSO-d₆ (deuterated dimethylsulfoxide) and tetramethylsilane (TMS) was used as the internal standard. The degree of sulfonation (DS) was determined by integration of distinct aromatic signals. The amount of water absorbed in the SPEEK membranes was determined by comparison of weights of a blotted soaked membrane and vacuum dried one. The water uptake was calculated with reference to the weight of the dry specimen: $(W_{wet}/W_{dry}-1) \times 100\%$.

[0032] The proton conductivity of the polymer membranes was measured by AC impedance spectroscopy using a Solartron® 1260 analyzer across 13 mm diameter samples clamped between two blocking stainless steel electrodes. The conductivity (σ) of the samples was calculated from the impedance data using the relation $\sigma = d/(R \cdot S)$ where d and S are the thickness and the face area of the sample respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the $\text{Re}(Z)$ axis. The impedance data were corrected for the contribution from the empty and short-circuited cell.

Result Analysis

[0033] Table 1 presents the results of the cross-linking procedure along with the conductivity values of the preparation of formulations of the different SPEEK samples tested and listed in FIG. 3.

[0034] Sample 1 with a DS of 1.0 was rendered completely cross-linked (insoluble in any solvent) only when cast from a water-acetone solution and with a glycerol content higher than one molecule per repeat unit of SPEEK (Sample 1b). When DMAc was used as casting solvent, none or only partial cross-linking occurred even at high glycerol concentration. The same was observed for all samples; no matter if they were low sulfonated (Samples 2a and 2b), medium sulfonated (Sample 8a) or highly sulfonated (Samples 1a, 3a, and 3b). When the cross-linker concentration was low, the membranes (Samples 1a, 1b, and 3) remained soluble even in cold water, which means that no cross-linking occurred. With a higher cross-linker concentration, these samples were partially soluble in DMAc which indicates that cross-linking was not complete. Similar observations applied for the casting solvent NMP (samples 4d and 9a). It is apparent that cross-linking was blocked by competing reaction of sulfonic acid groups with DMAc or NMP.

[0035] Recently it has been shown that DMAc and DMF form strong hydrogen bonding with sulfonated PEEK [G.P. Robertson, S.D. Mikhailenko, K.P. Wang, P.X. Xing, M.D. Guiver, and S. Kaliaguine, J. Membr. Sci.; S. Kaliaguine, S.D. Mikhailenko, K.P. Wang, P.X. Xing, G. Robertson, M.D. Guiver, Catalysis Today]. Moreover, both solvents have been found to be prone to thermally activated decomposition, accelerated by sulfonic acid functions and the produced

OR File No 6013-150USPR

dimethylamine also forms strong bonding with SPEEK. It is therefore preferable not to use these solvents for membrane casting. Preferable casting solvents for SPEEK with a DS above 0.8 are water and water-acetone mixtures. A water-alcohol mixture may also be used because there is little likelihood of hydroxyl interaction with acid groups due to the very low boiling point of ethanol, which is about 4° C under vacuum. This is sustained by the fact that the conductivity of a membrane cast from a water-alcohol solvent is not different from that of a membrane cast from a water-acetone solvent. Samples 6a and 6b of Table 1 are completely cross-linked when a high concentration of a polyol cross-linker was added to the casting solution.

[0036] It is interesting to note that the introduction of a polyol cross-linker did not change the sulfur content of the membranes treated at different temperatures. This can be seen by comparing curves c) and d) in FIG.1. However, the results of the titration turned out to be very different from the results of elemental chemical analysis for sulfur for the cross-linked samples. This can be seen by comparing curves a) and b) in FIG.1. The disparity between these two curves corresponds to the difference between the amount of sulfur comprised only in sulfonic acid functions (available for ion exchange as used in titration) and the total sulfur content, including bridging functions that are not detectable with a titration method.

[0037] Among the three cross-linkers used, the best membranes were obtained with ethylene glycol. They were stronger mechanically, flexible and less liable to deformation. Glycerol gave slightly less strong membranes, which sometimes were also less conductive than the membranes made with ethylene glycol as it can be seen by comparing, for example, samples 5b and 5c. Despite the fact that it also ensures SPEEK cross-linking, meso-erythrite is of no use as the membranes obtained were too brittle for any practical application (Samples 4a and 5a).

[0038] Therefore, the best cross-linked SPEEK membranes are obtained from SPEEK with a high degree of sulfonation, preferably between 0.75 and 1.0. Either water, water-acetone or a water-alcohol mixtures are used as a casting solvent. Any polyols can be used as cross-linker in a ratio above one molecule of cross-linker per SPEEK repeat unit. Preferably, ethylene glycol as a cross-linker is used in a ratio between 1.5 and 3 molecules per SPEEK repeat unit. Finally, the 18 wt% solution

containing the solvent and the cross-linker should be cast on a glass plate and dried at room conditions for two days, and then under vacuum for three days at a temperature gradually increasing from 25 to 180° C over two days, preferably between 25 and 150° C.

[0039] The swelling of a SPEEK membrane in water is commonly thought to be inversely related to its mechanical strength. In FIG. 4, room temperature water uptake along with conductivity are presented as a function of the DS as measured by titration (number of sulfonic acid functions per repeat unit). As can be seen from FIG.1, the sulfur contents measured by titration are lower than the whole sulfur concentration defined by elemental analysis and correspond obviously to the concentration of sulfonic acid groups available for ion exchange. From FIG. 4, it follows that the introduction of the ethylene-glycol cross-linker caused a decrease of the DS of sample 6 from 0.78 to 0.68. This is accompanied by more than twofold water uptake decrease from 79 to 32 wt%. At the same time, the conductivity decrease, from 2.7×10^{-2} to 1.4×10^{-2} S/cm, is not too significant and it remains within the limits where PEM is still suitable for fuel cell application. Starting from a DS of 0.71 (corresponding to a ratio [Ethylene-Glycol]/[SPEEK] of 1.97) membranes were completely cross-linked and even when swollen remained mechanically strong. Sample 5c having a DS of 0.96 was initially soluble in water and its water uptake may be taken as infinity. However at a ratio [Ethylene-Glycol]/[SPEEK] of 2.3 and higher it became fully cross-linked with water uptake below 70 wt% and a conductivity above 2×10^{-2} S/cm. It is important that these cross-linked membranes, which are rigid and strong at ambient conditions, become moldable and soft at temperatures above 150° C. This property makes it possible to prepare the membrane-electrode assemblies for FC.

[0040] The embodiment(s) of the invention described above is(are) intended to be exemplary only. The scope of the invention is therefore intended to be limited solely by the scope of the appended claims.

Table 1: Properties of the SPEEK membranes after the cross-linking procedure

Sample (DS) ^a	Solvent	Cross-linker	Cross-linker / SPEEK Ratio, mol/repeat unit	Cure condition		Conductivity, S/cm	Comments
				T, °C	Time, h		
1a (1.0)	DMAc	Glycerol	<1	125	36	-	Soluble in water
			>1	130	72	$\leq 1.5 \times 10^{-2}$	Partially soluble in DMAc, H ₂ O
1b (1.0)	Water + acetone	Glycerol	<1	125	48	-	Soluble in water
			>1	120	48	$\leq 2.5 \times 10^{-2}$	Complete cross-linking
2a (0.63)	DMAc	Ethylene-glycol	>1	125	48	-	Partially soluble in DMAc
2b (0.63)	DMAc	Glycerol	<1	125	48	$\leq 2 \times 10^{-3}$	Soluble in DMAc
			>1			$\leq 5.7 \times 10^{-3}$	Partially soluble in DMAc
3a (1.0)	DMAc	Glycerol	≈ 1	130	66	7.8×10^{-3}	Soluble in water
			>1	130	66	$\leq 1 \times 10^{-2}$	Partially soluble in DMAc
3b (1.0)	DMAc	Ethylene-glycol	>1	130	66	$\leq 1.5 \times 10^{-2}$	Partially soluble in DMAc
3c (1.0)	Water + acetone	Glycerol	>1	125	60	-	Complete cross-linking
4a (0.94)	Water	Meso-Erythritol	<1	135	60	-	Soluble in water
			>1	135	60	$\leq 2.2 \times 10^{-2}$	Complete cross-linking, brittle
4b (0.94)	Water	Ethylene-glycol	≈ 1.4	135	60	2.2×10^{-2}	Soluble in water
			1.4	135	60	$\leq 2.2 \times 10^{-2}$	Complete cross-linking
4c (0.94)	Water	Glycerol	2.6	135	60	2.2×10^{-2}	Complete cross-linking
4d (0.94)	NMP	Ethylene-glycol	<2.7	150	60	$\leq 4 \times 10^{-2}$	Soluble in hot water

Sample (DS)*	Solvent	Cross-linker	Cross-linker / SPEEK Ratio, mol/repeat unit	Cure condition		Conductivity, S/cm	Comments
				T, °C	Time, h		
5a (0.96)	Water	Meso-Erythritol	0.5-0.9	140	48	-	Soluble in water
			1-2	140	48	-	Cross-linked, brittle
5b (0.96)	Water	Glycerol	>1	140	48	$\leq 1.2 \times 10^{-2}$	Complete cross-linking
5c (0.96)	Water	Ethylene-Glycol	≤ 1.5	140	48	$\leq 2.2 \times 10^{-2}$	Soluble in water at 100°C
			>1.5	140	48	$\leq 2.7 \times 10^{-2}$	Complete cross-linking
6a (0.78)	Water+ Alcohol	Ethylene-Glycol	0.6	140	60	-	Soluble in water
			>1.6	140	60	$\leq 2.5 \times 10^{-2}$	Complete cross-linking
6b (0.78)	Water + acetone	Ethylene-Glycol	<1.5	140	60	$\leq 1.6 \times 10^{-2}$	Soluble in water at 100°C
			>1.5	140	60	$\leq 2.5 \times 10^{-2}$	Complete cross-linking
7 (0.90)	Water + Alcohol	Ethylene-Glycol	>1.6	140	60	$\leq 4.2 \times 10^{-2}$	Complete cross-linking
8a (0.78)	DMAc	Ethylene-Glycol	<1	150	68	-	Soluble in DMAc, hot water
			>1	150	68	-	Partially soluble in DMAc
8c (0.78)	Water+ Alcohol	Ethylene-Glycol	>1.5	150	68	$\leq 2.6 \times 10^{-2}$	Complete cross-linking
9a (0.83)	NMP	Ethylene-Glycol	1.65-3.3	150	68	$\leq 4.6 \times 10^{-2}$	Soluble in water at 100°C
9b (0.83)	Water+ Alcohol	Ethylene-Glycol	<1.9	150	68	$\leq 6.5 \times 10^{-2}$	Soluble in water at 100°C
			>1.9	150	68	$\leq 4 \times 10^{-2}$	Complete cross-linking

*Measured by NMR before membrane casting

WE CLAIM:

1. A method for the preparation of a cross-linked proton exchange membrane, comprising:
providing a sulfonated polymer;
dissolving the polymer in a polar casting solvent;
adding at least one cross-linker agents selected from the group consisting of polyols and diols, the cross-linker agent being added in a sufficient ratio of polyol molecules per repeat unit of the sulfonated polymer to generate cross-linking;
casting the solution to obtain the membrane; and
curing the membrane.
2. A method in accordance with claim 1, wherein the membrane is cured under vacuum.
3. A method in accordance with claim 1, wherein the sulfonated polymer is sulfonated polyether ether ketone.
4. A method in accordance with claim 1, wherein the polar casting solvent is selected from the group consisting of DMAc, NMP, DMF, butyrolactone, water, a mixture of water and acetone and a mixture of water and alcohol.
5. A method in accordance with claim 4, wherein the polar casting solvent is selected from the group consisting of water, a mixture of water and acetone and a mixture of water and alcohol.
6. A method in accordance with claim 1, wherein the cross-linker is selected from the group consisting of ethylene glycol and glycerol.

7. A method in accordance with claim 1, wherein the sulfonated polymer has a degree of sulfonation higher than 0.6.
8. A method in accordance with claim 7, wherein the degree of sulfonation is above 0.75.
9. A method in accordance with claim 1, wherein the curing is carried out at a temperature that is gradually increased.
10. A method in accordance with claim 9, wherein the curing temperature range between 25 and 180° C.
11. A method in accordance with claim 10, wherein the curing temperature range between 25 and 150° C.
12. A cross-linked proton exchange membrane prepared in accordance with claim 1.
13. A fuel cell using a cross-linked proton exchange membrane prepared in accordance with claim 1.

ABSTRACT

The present invention concerns a new method for the preparation of proton exchange membranes based on cross-linked sulfonated polymers, preferably cross-linked polyether ether ketones (SPEEK). The method of the present invention consists in thermally activating bridging of the polymer chains with diol or polyols as cross-linkers. The addition of diol or polyols makes the resulting polymer stronger and reduces its swelling by water without a substantial reduction in proton conductivity. It also concerns proton exchange membranes made by the method of the present invention.

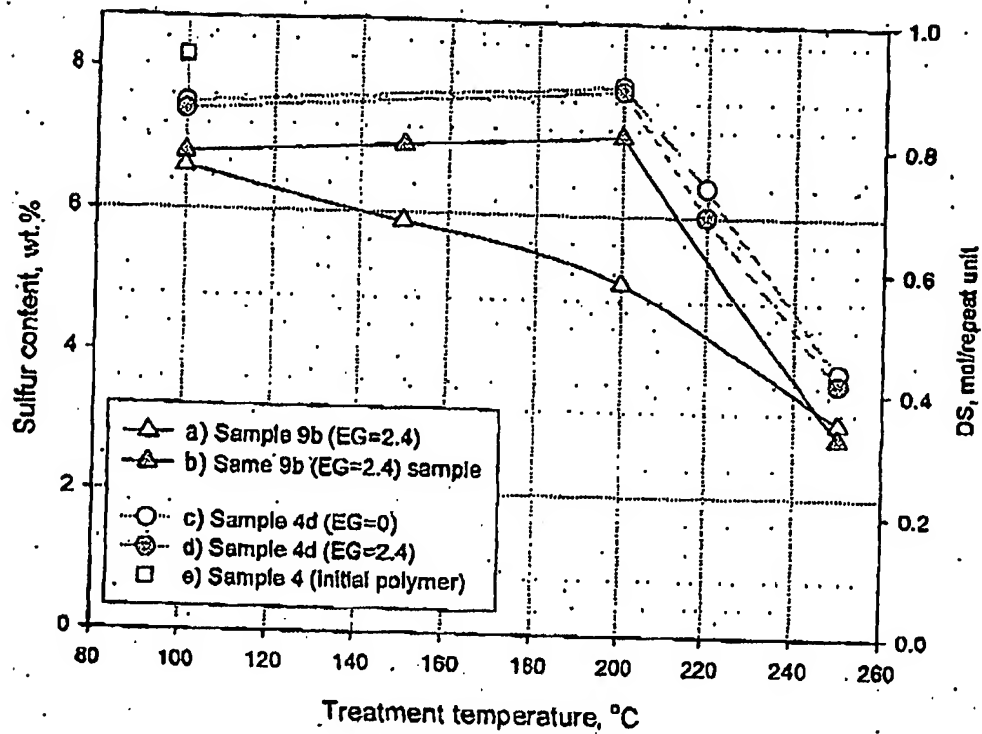
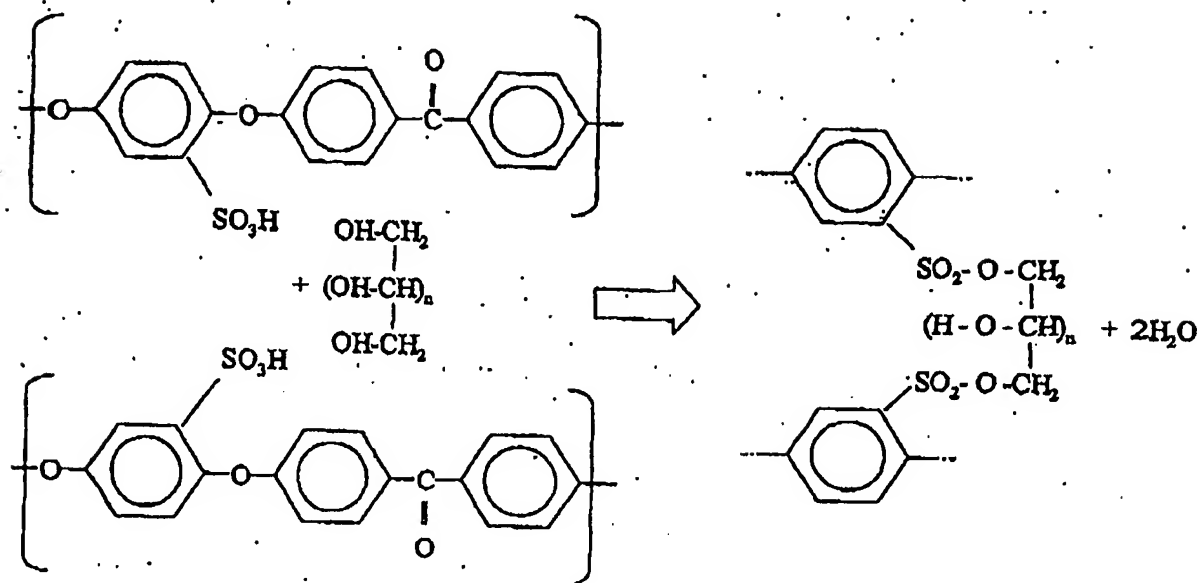


FIGURE 1

BEST AVAILABLE COPY



n = 0 - Ethylene Glycol
n = 1 - Glycerine
n = 2 - Erythrite

FIGURE 2

BEST AVAILABLE COPY

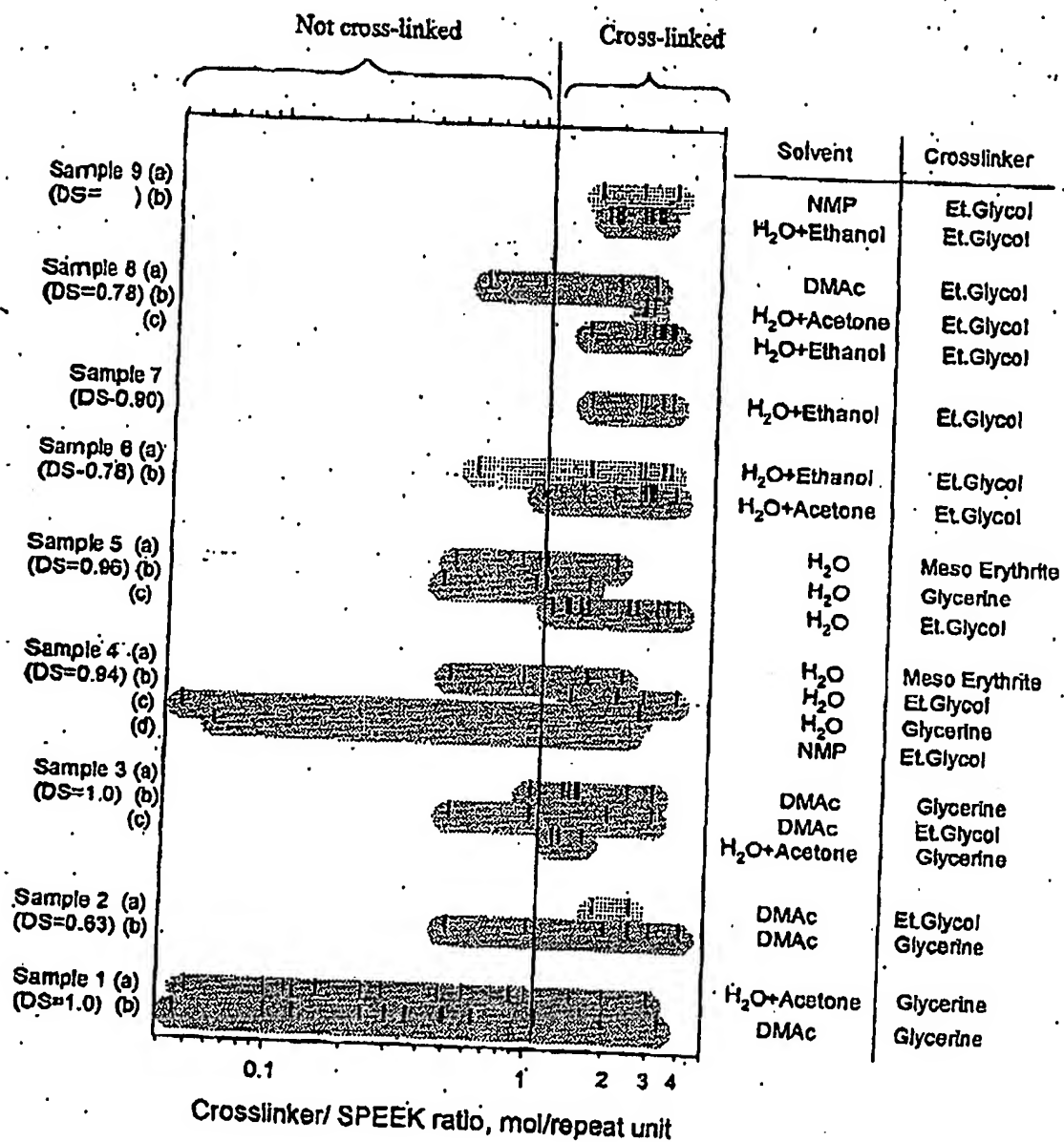


FIGURE 3

BEST AVAILABLE COPY

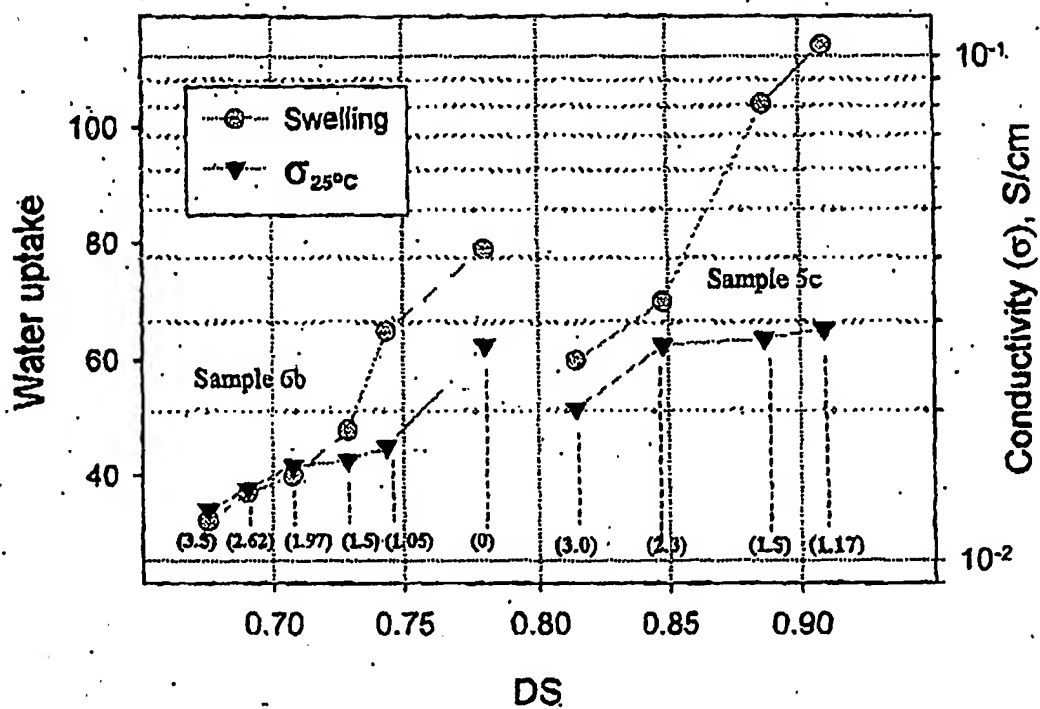


FIGURE 4

BEST AVAILABLE COPY